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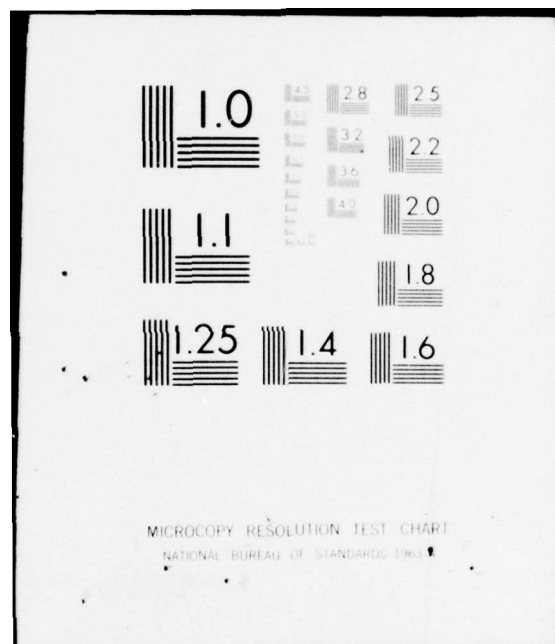
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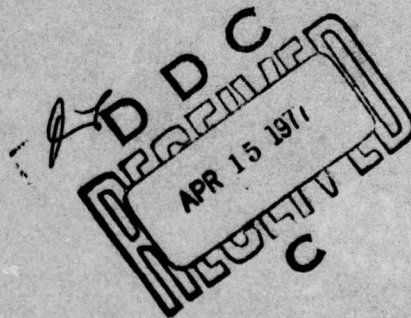
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REPORT NO. 1972

THE EFFECTS OF UNCERTAINTIES IN THE
TWO-BODY ION-ION RECOMBINATION
COEFFICIENT UPON COMPUTED ION DISTRIBUTIONS
IN THE STRATOSPHERE AND MESOSPHERE

Joseph M. Heimerl

March 1977



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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER BRL REPORT NO. 1972	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) THE EFFECTS OF UNCERTAINTIES IN THE TWO-BODY ION-ION RECOMBINATION COEFFICIENT UPON COMPUTED ION DISTRIBUTIONS IN THE STRATOSPHERE AND MESO- SPHERE	5. TYPE OF REPORT & PERIOD COVERED Final rept.	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR Joseph M. Heimerl	8. CONTRACT OR GRANT NUMBER(s)	
9. PERFORMING ORGANIZATION NAME AND ADDRESS US Army Ballistic Research Laboratory Aberdeen Proving Ground, Maryland 21005	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS DNA Subtask S990AXHD010 and DARCOM RDT&E No. 11L161102B53A	
11. CONTROLLING OFFICE NAME AND ADDRESS US Army Materiel Development & Readiness Command 5001 Eisenhower Avenue Alexandria, VA 22333	12. REPORT DATE MARCH 1977	13. NUMBER OF PAGES 24
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) (12) 18p.	15. SECURITY CLASS. (of this report) Unclassified	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) VLF Communication VLF Attenuation Ion-ion Recombination Ion-neutral Collision Frequency		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) (real) A version of the AIRCHEM code (BENCHMARK-76) has been used to study the sensitivity of the daytime ionic populations to decade changes in selected values of the two-body ion-ion recombination rate coefficient over the altitude range 30-80 km, inclusive. At one extreme, computed ionic populations change by as much as a factor of two in isolated cases. At the other extreme much smaller changes are computed.		

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I. INTRODUCTION

There exist phenomena, such as solar proton events and nuclear explosions, that can severely disturb the total charge content of the atmosphere. In the altitude interval 30-80 km these disturbances can affect systems over a wide range of the electromagnetic spectrum, e.g., disruption of radar and communications operations. The rate at which the disturbed atmosphere returns to normal depends on the processes for removing the excess charge. At the higher altitudes (70-80 km) electron-ion recombination occurs faster than negative ion formation and so charge neutralization is dominated by the electron-ion dissociation recombination process. At lower altitudes (~ 60 km) negative ion formation permits ion-ion mutual neutralization to compete with and (still lower) to dominate electron-ion dissociative recombination. (The precise times and altitudes at which this dominance occurs is a function of the intensity of the disturbance as well as the rates of the recombination processes. In this report we shall focus on the ion-ion mutual neutralization process for fixed excitation conditions and so reported times and altitudes would have to be adjusted for other disturbing conditions.)

For ELF/VLF communications, Field and Dore¹ have found that the largest uncertainties in these attenuation rates (several dB per megameter) can be attributed to uncertainties in the positive ion - negative ion recombination rate coefficient, α_i .^{*} They have also found that at VLF uncertainties in the ion-neutral collision frequency, ν_i , can cause uncertainties in attenuation about equal to that found for uncertainties in α_i .

These two parameters are indirectly related. ν_i is a function of the ion distribution.^{**} This distribution is determined in part by the recombination coefficient. The question that arises is whether or not the operational uncertainties due to ν_i and to α_i can be treated as separate, independent problems. To restate this problem: What is the change in the ion species distribution for a given change in α_i ?

^{*}The subscript "i" refers to "ion" as opposed to electron.

^{**}For one ion species and one neutral species $\alpha_i \propto A^2 \mu^{-1/2}$, where A is the sum of the molecular and ionic radii and μ is the reduced mass of the colliding ion and molecule. (Field, private communication quoting Propagation of Electromagnetic Waves in a Plasma by Ginzberg, trans. by Roger and Roger, Gordon and Breach Publishers, N.Y., p. 97.)

¹E. C. Field and M. N. Dore, private communication, 1976.

Though some information regarding α_j has been determined from analysis of natural and nuclear disturbances, much reliance has been placed on model predictions. The AIRCHEM code² has been used at the BRL to predict the response of the ionosphere to disturbed conditions and as such it provides us with a convenient tool for examining the sensitivity of ionic populations to variation in values of individual two body ion-ion recombination rate coefficients, α_j . We distinguish between an effective ion-ion recombination coefficient, α_i , and the coefficient for the j th recombination, α_j . α_i is a weighted sum of the α_j , $\alpha_i = \sum_j n_j^+ n_j^- \alpha_j / \sum_j n_j^+ n_j^-$, where n_j^+ and n_j^- are the positive and negative ion densities of the j th recombination reaction.

This report describes: our current state of knowledge about the values of α_j (section II), the procedure used in those sensitivity tests and the computed changes in the ion populations for changes in selected values of α_j , under fixed disturbing conditions (section III).

II. VALUES FOR THE TWO BODY ION-ION RECOMBINATION COEFFICIENT, α_j

This topic has been reviewed in 1972³ and 1974,⁴ and will be dealt with briefly here. Room temperature values of the recombination coefficient for eight pairs of ions of atmospheric interest are listed in Table I. The salient feature to be gleaned from Table I is the wide range of disagreement for all ion pairs except $O_2^+ + NO_3^-$ and $O_2^+ + O^-$. Values differ by about a factor of ten in two cases.

²E. L. Lortie, M. D. Kregel and F. E. Niles, "AIRCHEM: A Computational Technique for Modeling the Chemistry of the Atmosphere," BRL Report No. 1913, 1976. (AD #A030157)

³B. H. Mahan, "Recombination of Gaseous Ions," in Advances in Chemical Physics 23, 1-40, 1973, Ed. by I. Prigogine and S. A. Rice.

⁴J. T. Moseley, R. E. Olson and J. R. Peterson, "Ion-Ion Neutralization," Case Studies in Atomic Physics 5, 1-45, 1975.

⁵M. N. Hirsh and P. N. Eisner, "Laboratory Measurements of Ion Chemistry in a Simulated Disturbed Ionosphere," Radio Sci. 7, 125-131, 1972.

⁶D. Smith and M. J. Church, "Binary Ion-Ion Recombination Coefficients Determined in a Flowing Afterglow Plasma," International Journal of Mass Spectrometry and Ion Physics, 19, 185-200, 1976.

⁷B. H. Mahan and J. C. Person, "Gaseous Ion Recombination Rates," J. Chem. Phys. 40, 392-401, 1964.

⁸R. E. Olson, "Absorbing Sphere Model for Calculating Ion-Ion Recombination Total Cross Sections," J. Chem. Phys. 56, 2979-2984, 1972.

⁹M. N. Hirsh and P. N. Eisner, "Two-Body Recombination of O_2^+ and O_2^- in Low-Pressure Oxygen," Bull. Am. Phys. Soc. 17, 395, 1972.

¹⁰M. N. Hirsh, "Ion Chemistry in Electron-Inactivated Air: Comparison of Experiment with Theory," Bull. Am. Phys. Soc. 21, 165, 1976.

TABLE 1. VALUES OF TWO-BODY RECOMBINATION COEFFICIENTS OF ATMOSPHERIC INTEREST

<u>System</u>	$\alpha_j(300^\circ\text{K})$ ($\times 10^{-7} \text{ cm}^3/\text{s}$)	<u>Ref</u>	<u>Remarks</u>
1. $\text{NO}^+ + \text{NO}_2^-$	5.1 ± 1.5	4	mb
	1.75 ± 0.6	5	sa
	3.5		A, average of Ref's 4 & 5
	0.64 ± 0.07	6	Lpfa
	2.1 ± 0.6	7	Sa, value refers to $\text{NO}^+(\text{NO})$ & $\text{NO}_3^-/\text{NO}_2^-$, Ref. 3
	1.2 ± 0.3	8	Cal
2. $\text{NO}^+ + \text{NO}_3^-$	8.1 ± 2.3	4	mb
	0.34 ± 0.12	5	Value refers to NO^+ & $\text{NO}_3^-/\text{NO}_2^-(\text{H}_2\text{O})$, Ref. 10
	4.0		A, average of Ref.'s 4 & 5
	0.57 ± 0.6	6	Lpfa
	1.1 ± 0.3	8	Cal
3. $\text{NO}^+ + \text{O}^-$	4.9 ± 2.0	4	mb, A
	1.9 ± 0.6	8	Cal
4. $\text{NO}^+ + \text{O}_2^-$	5.8 ± 1.0	4	mb, A
	2.4 ± 0.8	8	Cal
5. $\text{O}_2^+ + \text{NO}_2^-$	4.1 ± 1.3	4	mb, A
	1.2 ± 0.3	8	Cal
6. $\text{O}_2^+ + \text{NO}_3^-$	1.3 ± 0.4	4	mb, A
	1.0 ± 0.2	8	Cal
7. $\text{O}_2^+ + \text{O}^-$	1.0 ± 0.4	4	mb, A
	1.0 ± 0.2	8	Cal
8. $\text{O}_2^+ + \text{O}_2^-$	4.2 ± 1.3	4	mb, A
	1.0 ± 0.1	9	sa
	2.4 ± 0.8	8	Cal

mb = merged beam

sa = stationary afterglow

A = values used in AIRCHEM code

Lpfa = Langmuir probe/flowing afterglow

Cal = calculation

The following illustrates the difficulties involved in these experiments. Recent measurements¹¹ of $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3 + \text{NO}_3^-$ and $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3 + \text{NO}_3^-(\text{HNO}_3)$ yield recombination coefficients of $(0.55 \pm 0.10) \times 10^{-7} \text{ cm}^3/\text{s}$ and $(0.57 \pm 0.10) \times 10^{-7} \text{ cm}^3/\text{s}$, respectively. However, the negative ion concentrations were mixed with unknown concentrations of: $\text{NO}_2^-/\text{NO}_2^-(\text{H}_2\text{O})/\text{NO}_3^-(\text{H}_2\text{O})$ ions and $\text{NO}_3^-(\text{H}_2\text{O})/\text{NO}_3^-(\text{HNO}_3)_2$ ions, respectively. The authors argue that because the lower earth's atmosphere ought to contain mixtures of similar ions, these values of α_j should be representative of the effective α_j in the earth's stratosphere. The work of Goldberg *et al.*¹² tends to support this notion. They require an effective α_j of the order of $5 \times 10^{-8} \text{ cm}^3/\text{s}$ at 60 km to explain ion-pair production by the x-ray star Sco X-1.

Appeal to more direct atmospheric measurements¹³ sheds little light on reducing the range of values. Ulwick's analysis¹³ of the 1969 solar proton event shows that the derived effective recombination coefficient can vary from a high of $\sim 1.5 \times 10^{-7} \text{ cm}^3/\text{s}$ at 45 km to a low of $\sim 4 \times 10^{-8} \text{ cm}^3/\text{s}$ at 70 km. Moreover, he has estimated that each of his data points is accurate to a factor of two, leading again to a total spread of about a factor of ten.

An examination into the sources of these real or apparent discrepancies is beyond the scope of this report. It is sufficient for our purposes to note that a factor of 10 variation in a nominal value for α_j appears to be reasonable.

The values for α_j used in the AIRCHEM code are designated by an α_3 "A" in Table I. All other α_j were assigned a value of $2.0 \times 10^{-7} \text{ cm}^3/\text{s}$ at 300°K and all the α_j were assigned the weak temperature dependence of T^{-2} .¹⁴

¹¹D. Smith, N. G. Adams and M. J. Church, "Mutual Neutralization Rates of Ionospherically Important Ions," *Planet. Space Sci.* 24, 697-703, 1976.

¹²R. A. Goldberg, W. H. Jones, P. R. Williamson, J. R. Barcus and L. C. Hale, "Equatorial X-Rays and Their Effect on the Lower Mesosphere," to be published *J. Atmos. Terr. Phys.*

¹³J. C. Ulwick, "Effective Recombination Coefficients and Lumped Parameters in the D-Region During Solar Particle Events," *Proceedings of COSPAR Symposium on Solar Particle Event of November 1969*, AFCRL Special Report No. 144, 571-587, 1972. Ed. by J. C. Ulwick.

¹⁴DNA Reaction Rate Handbook, 2nd Ed., March 72, Table 241, V. (Revision No. 3, September 1973).

III. RESULTS AND DISCUSSION

The AIRCHEM code,² tailored for nuclear atmospheric disturbances, was used for the sensitivity tests. This code consists of electrons, 15 negative ion species, 27 positive ion species and 21 neutral species. Only the first hydrate of O_2 , CO_3 , CO_4 , NO_2 and NO_3 are considered. The heaviest and "terminal"² negative ion used in this code is NO_3^- (HNO_3). Nighttime mass spectrometer flights through the D-region have indicated that other negative ions exist in the atmosphere.¹⁵⁻¹⁷ Such ions have not been considered in this model.

A nominal set of 495 reactions is used to describe the ion and neutral chemistry. Negative ion photodestruction has been included by considering the cross section for the reaction to be 10^{-18} cm² for wavelengths shorter than the negative ion's electron affinity and zero elsewhere. Our wavelength region of interest is $760.0 > \lambda > 100.0$ nm and the solar flux used corresponded to midlatitude overhead sun conditions. (Recent computations using measured cross sections have not revealed any substantial changes.) Positive ion photodestruction is not considered in this set of reactions.

The excitation conditions chosen and fixed for these sensitivity tests are thought to be typical rather than extreme. To wit, we have used for prompt ionization, $N_e = 10^{11}$ electrons/cm³. The delayed ionization is given by $Q(t) = Q_0(1 + t)^{-1.2}$, where t is the time in seconds and we have selected $Q_0 = 10^8$ ion-pairs/cm³/s. Partitioning of the charge closely follows Gilmore,¹⁸ except that $N_2(A^3\Sigma)$ is not considered, and that production of $O_2(^1\Delta)$ and O are taken as 0.25 and 1.28 per ion-pair per second, respectively. Daytime neutral densities are taken from CIRA 1972,¹⁹ U.S. Standard Atmosphere 1962²⁰ and other literature sources and extrapolations.²¹

- ¹⁵R. S. Narcisi, A. D. Bailey, L. Della Lucca, C. Sherman and D. M. Thomas, "Mass Spectrometric Measurements of Negative Ions in the D- and lower E-Regions," *J. Atmos. Terr. Phys.* **33**, 1147-1159, 1971.
- ¹⁶F. Arnold, J. Kissel, D. Krankowsky, H. Weider and J. Zähringer, "Negative Ions in the Lower Ionosphere: A Mass-Spectrometric Measurement," *J. Atmos. Terr. Phys.* **33**, 1169-1175, 1971.
- ¹⁷F. Arnold and D. Krankowsky, "Negative Ions in the Lower Ionosphere: A Comparison of a Model Computation and a Mass-Spectrometer Measurement," *J. Atmos. Terr. Phys.* **33**, 1693-1702, 1971.
- ¹⁸F. Gilmore as quoted by B. F. Myers and M. R. Schoonover, "Electron Energy Degradation in the Atmosphere: Consequent Species and Energy Densities, Electron Flux, and Radiation Spectra," *DNA 3513T*, 3 Jan 75, Table 6.
- ¹⁹K. S. W. Champion and R. A. Schweinfurth, "A New Mean Reference Atmosphere for 25 to 500 km," *AFCRL-72-0579*, 2 Oct 72; The Mean COSPAR International Reference Atmosphere 1972" in *COSPAR International Reference Atmospheres 1972*, Akademie Verlag, Berlin, 1972.
- ²⁰United States Committee on Extension to the Standard Atmosphere, *U.S. Standard Atmosphere, 1962*, U.S. Government Printing Office, Washington, D.C., Dec 62.
- ²¹F. E. Niles, private communication.

We caution that the AIRCHEM code has been validated only for quiet or undisturbed daytime conditions and then only for ²²electron, total positive ion and total negative ion concentrations. This code has not been validated either at the level of excitation or disturbing conditions or at the scale of individual ion species concentrations used here.

In the code each of 15 positive ions is permitted to recombine with 14 different negative ions, leading to 210 recombination coefficients. Resources did not permit the systematic variation of all possible combinations, nor was this approach deemed necessary. Since almost all values of α_i are identical we can identify the dominant contributions to the sum defining α_i by noting the computed dominant ion species concentrations.

For a given altitude the AIRCHEM code computes ion concentrations as a function of time after the initiation of the disturbance. At each decade of time (10^0 through 10^4 seconds, inclusive) the dominant positive ion(s) and dominant negative ions are identified. Pairing of these positive and negative ionic species then determines the ion-ion recombination reactions whose coefficients are to be varied. Table 2 shows these recombination reactions as a function of altitude. The corresponding rate coefficients were varied by multiplying α_i by 10 and 1/10. (The discussion in section II indicates that for nominal values of $\alpha_i \sim 10^{-7}$ cm³/s, decreasing the value is more realistic than increasing the value. The increased value has been retained for completeness.) The code was re-run for each of these two cases and the ion concentrations again examined. These results are shown in Table 3.

The information content of this table is quite high and requires a bit of explanation. The altitude is listed vertically to the extreme left and the decades of time after the initiation of the disturbance are listed horizontally across the top of the table. The area within the table located by an altitude and a time coordinate is occupied by two columns of ionic species, one positive, the other negative. To the immediate right of each ion species is a number with a superscript and a subscript. This number shows the percentage contribution of that ionic species to the total ion population for nominal values of α_i . The superscript (subscript) when added to the physically larger number reveals the percentage contribution of that ionic species to the total ion population for the selected values of α_i (see Table 2) multiplied by 10 (1/10).

For example, at an altitude of 60 km and at 10^2 seconds, the species NO_3^- constitutes 34% of the total negative ion population for nominal values of α_i . For values of $\alpha_i \times 10$ ($\times 1/10$) NO_3^- constitutes 19% (38%) of the total negative ion population.

²²J. M. Heimerl and F. E. Niles, "Modeling of Charged Particle Chemistry in the Stratosphere and Mesosphere," Trans. Am. Geophys. Union 57, 303, 1976.

TABLE 2. DOMINANT RECOMBINATION REACTIONS TAKEN FROM BENCHMARK-76 RESULTS; NOMINAL VALUES OF α_j HAVE BEEN USED.

<u>ALT (km)</u>	<u>Dominant Recombination Reactions</u>
80	$\text{NO}^+ + \text{O}_2^-$ $\text{NO}^+ + \text{NO}_2^-$
70	$\text{NO}^+ + \text{O}_2^-$ $\text{NO}^+ + \text{NO}_3^-$ $\text{NO}^+(\text{H}_2\text{O}) + \text{NO}_3^-$ $\text{NO}^+(\text{H}_2\text{O})_2 + \text{NO}_3^-$
60	$\text{NO}^+ + \text{O}_2^-$ $\text{NO}^+ + \text{CO}_3^-$ $\text{NO}^+(\text{H}_2\text{O})_2 + \text{NO}_3^-$ $\text{NO}^+(\text{H}_2\text{O})_3 + \text{NO}_3^-$
50	$\text{NO}^+(\text{H}_2\text{O}) + \text{CO}_3^-$ $\text{H}^+(\text{H}_2\text{O})_3 + \text{CO}_3^-$ $\text{H}^+(\text{H}_2\text{O})_3 + \text{NO}_3^-$
40	$\text{H}^+(\text{H}_2\text{O})_4 + \text{CO}_3^-$ $\text{H}^+(\text{H}_2\text{O})_4 + \text{NO}_3^-(\text{HNO}_3)$ $\text{H}^+(\text{H}_2\text{O})_4 + \text{NO}_3^-(\text{H}_2\text{O})$
30	$\text{H}^+(\text{H}_2\text{O})_4 + \text{NO}_3^-(\text{H}_2\text{O})$ $\text{H}^+(\text{H}_2\text{O})_4 + \text{NO}_3^-(\text{HNO}_3)$

ALT/TIME	10^0 s				10^1 s			
<u>80 km</u>	O_2^-	72_{-14}^6	NO^+	76_3^3	O_2^-	72_{-12}^9	NO^+	76_0^0
	O^-	16_{-3}^3	O_2^+	20_1^1	O^-	18_{-3}^2	O_2^+	22_2^2
	NO_2^-	13_{-16}^{-11}			NO_2^-	10_{-12}^{-8}		
<u>70 km</u>	O_2^-	93_0^{-1}	NO^+	78_0^1	O_2^-	89_0^1	NO^+	75_0^0
			O_2^+	18_0^0			O_2^+	20_0^0
<u>60 km</u>	O_2^-	73_1^2	NO^+	71_0^{-3}	O_2^-	56_1^1	NO^+	56_0^{-4}
	CO_3^-	15_1^{-3}	O_2^+	11_0^1	CO_3^-	30_0^{-2}	$NO^+(H_2O)$	14_0^{-1}
							O_2^+	9_0^1
<u>50 km</u>	CO_3^-	42_1^{-2}	$NO^+(H_2O)$	29_0^{-7}	CO_3^-	55_1^2	$NO^+(H_2O)$	36_0^{-9}
	O_2^-	19_0^1	NO^+	27_0^3	NO_3^-	15_2^{-4}	$H^+(H_2O)_3$	18_{-1}^{-1}
	NO_3^{-*}	12_0^2	$H^+(H_2O)_2$	11_0^2			$NO^+(H_2O)_2$	14_1^{-3}
	CO_4^-	10_0^0					$H^+(H_2O)_2$	11_{-1}^5
							NO^+	9_{-1}^4
<u>40 km</u>	CO_3^-	47_{-3}^{-3}	$H^+(H_2O)_4$	58_7^{-28}	$CO_3^-(H_2O)$	31_9^{-15}	$H^+(H_2O)_4$	67_4^{-14}
	$CO_3^-(H_2O)$	31_8^{-15}	$H^+(H_2O)_3$	18_1^{-6}	CO_3^-	31_0^{-4}	$H^+(H_2O)_3$	19_0^{-3}
	$NO_3^-(H_2O)$	11_{-4}^9	$NO^+(H_2O)_2$	14_{-7}^{19}	$NO_3^-(H_2O)$	27_{-6}^{18}	$NO^+(H_2O)_2$	8_{-3}^9
<u>30 km</u>	$CO_3^-(H_2O)$	69_{11}^{-31}	$H^+(H_2O)_4$	71_4^2	$CO_3^-(H_2O)$	58_5^{-19}	$H^+(H_2O)_4$	75_2^1
	$NO_3^-(H_2O)$	19_{-7}^{28}	$H^+(H_2O)_5$	23_0^0	$NO_3^-(H_2O)$	29_{-7}^{19}	$H^+(H_2O)_5$	23_0^0
					$NO_3^-(HNO_3)$	10_2^{-5}		

TABLE 3. PERCENTAGE CONTRIBUTION OF LISTED ION TO THE TOTAL ION POPULATION AS A FUNCTION

$10^2 s$				$10^3 s$				$10^4 s$			
O_2^-	52_{-19}^{15}	NO^+	91_0^0	NO_2^-	41_{13}^{-29}	NO^+	95_0^0	NO_2^-	44_6^{-26}	NO^+	88_0^0
NO_2^-	24_{27}^{-20}			O_2^-	32_{-11}^{25}			O_2^-	30_{-7}^{27}		
O^-	22_{-8}^6			O^-	15_{-5}^{12}			NO_3^-	18_3^{-10}		
				NO_3^-	10_4^{-7}			O^-	8_{-2}^7		
O_2^-	68_{-9}^3	NO^+	78_0^0	O_2^-	42_{-17}^{18}	NO^+	59_0^0	NO_3^-	57_{10}^{-34}	NO^+	31_0^0
CO_3^-	18_{-7}^{-4}	$NO^+(H_2O)$	10_0^0	NO_3^-	34_{25}^{-28}	$NO^+(H_2O)$	25_0^0	O_2^-	19_{-5}^{14}	$NO^+(H_2O)_2$	25_1^0
NO_3^-	5_{17}^1			CO_3^-	12_{-5}^5			NO_2^-	15_{-4}^{11}	$NO^+(H_2O)$	23_0^0
								CO_3^-	6_0^8		
CO_3^-	41_0^{10}	NO^+	32_0^{-1}	NO_3^-	63_9^{-26}	$NO^+(H_2O)_2$	38_1^{-4}	NO_3^-	71_6^{-24}	$H^+(H_2O)_3$	38_2^{-3}
NO_3^-	34_4^{-15}	$NO^+(H_2O)$	23_0^{-2}	CO_3^-	16_{-4}^{19}	$NO^+(H_2O)$	18_0^0	NO_2^-	9_{-3}^{10}	$H^+(H_2O)_4$	25_1^{-1}
O_2^-	15_0^5	$NO^+(H_2O)_2$	18_0^{-1}			$H^+(H_2O)_3$	14_0^{-1}	CO_3^-	6_1^7	$NO^+(H_2O)_2$	24_{-2}^0
		$H^+(H_2O)_2$	14_0^{-1}			$H^+(H_2O)_2$	9_0^3			$NO^+(H_2O)$	9_{-1}^1
CO_3^-	41_{-4}^4	$H^+(H_2O)_3$	43_6^{-13}	NO_3^-	47_3^{-6}	$H^+(H_2O)_3$	53_9^{-22}	NO_3^-	49_1^{-4}	$H^+(H_2O)_3$	62_6^{-25}
NO_3^-	37_5^{-10}	$NO^+(H_2O)$	32_{-8}^2	$NO_3^-(H_2O)$	32_{-1}^2	$NO^+(H_2O)$	26_{-7}^{13}	$NO_3^-(H_2O)$	43_{-2}^0	$NO^+(H_2O)$	20_{-6}^{17}
$NO_3^-(H_2O)$	17_{-1}^1	$NO^+(H_2O)_2$	13_{-3}^2	CO_3^-	15_{-2}^7	$NO^+(H_2O)_2$	11_{-3}^6			$NO^+(H_2O)_2$	8_{-1}^8
$NO_3^-(H_2O)$	67_{-6}^6	$H^+(H_2O)_4$	77_{-4}^{-5}	$NO_3^-(H_2O)$	71_{-3}^8	$H^+(H_2O)_4$	76_0^{-1}				
$CO_3^-(H_2O)$	12_{-1}^{-6}	$H^+(H_2O)_3$	21_{-1}^{-1}	$NO_3^-(HNO_3)$	14_2^{-7}	$H^+(H_2O)_3$	21_0^0				
NO_3^-	12_{-1}^{-1}										
$NO_3^-(HNO_3)$	38_{-6}^{-16}	$H^+(H_2O)_4$	79_{-3}^{-3}								
$CO_3^-(H_2O)$	34_{-5}^2	$H^+(H_2O)_5$	24_0^0								
$NO_3^-(H_2O)$	30_{-5}^{12}										

OF ALTITUDE, TIME AND CHANGES IN SELECTED VALUES OF α_j . (See text for discussion.)

The values in Table 3 are given in percent of total ion population to account for the fact that changing values of α_j can alter the total ion concentrations. Thus changes in the species distributions are more easily read from this table. Code predicted absolute values can be recovered for each entry in Table 3 by multiplying by the appropriate total ion concentrations (in cm^{-3}) listed in Table 4. The key "MAX," "NOM," and "MIN" correspond to the cases $\alpha_j \times 10$, α_j and $\alpha_j \times 1/10$, respectively.

This version of the AIRCHEM code computes $\alpha_j' = \alpha_j + \alpha_{3B} \times [M]$, where α_j is the two body ion-ion recombination coefficient (of interest in this study), α_{3B} is the three body ion-ion recombination coefficient and $[M]$ is the total neutral concentration at a given altitude. Since only α_j has been varied, the effect of $\alpha_{3B} \times [M]$ must be accounted for. From Cole and Pierce's²³ "selected value" for their ion-ion recombination coefficient at ground level the value $8 \times 10^{-26} \text{ cm}^6/\text{s}$ can be derived for α_{3B} . This value is such that $\alpha_j' \approx \alpha_j$ except at 30 km where $\alpha_j/10 \approx \alpha_{3B} \times [M]$. This case was re-computed with α_{3B} set equal to zero. Trivial changes (0-3 percentage points) were found in the computed ion distributions of Table 3 and small changes (12-15%) were found in the total ion concentrations of Table 4. Thus, no corrections for the inclusion of the three body ion-ion recombination have been made to the values listed in Tables 3 and 4.

In Table 4 at 70 and 80 km altitudes, large differences exist between the sum of the positive and sum of the negative ions. Since charge is conserved in the AIRCHEM code, this difference defines the electron density, and shows that electron-ion recombination does dominate at the higher altitudes. As we progress lower in altitude (and/or later in time) the sum of the negative ions approaches, then approximately equals the sum of the positive ions. Thus for our choice of excitation conditions, ion-ion recombination becomes important at 60 km and dominates below 50 km.

Referring to Table 3 we find no case which shows more than a factor of about two change in a dominant ion species. Specifically see $\text{H}^+(\text{H}_2\text{O})_4$ at 40 km and $\text{CO}_3^-(\text{H}_2\text{O})$ at 30 km both at 10^0 seconds. These changes are for the less likely increase in α_j ; the more likely decrease indicates rather small changes in the ionic distributions for altitudes 60 km and below.

The AIRCHEM code has been used as a tool to study the sensitivity of distributions to changes in selected values of individual two body ion-ion recombination coefficients. We caution that the code has not been validated for the conditions or in the detail used herein, and that the

²³R. K. Cole, Jr. and E. T. Pierce, "Electrification in the Earth's Atmosphere for Altitudes Between 0 and 100 Kilometers," J. Geophys. Res. 70, 2735-2749, 1965.

ion species used are a sub-set of those detected in the atmosphere. With these points in mind we find the results of this limited study indicate that for altitudes lower than ~ 60 km, one extreme value of the ion-ion recombination coefficient, $\alpha_j \times 10$, can change ionic populations by as much as a factor of two, in isolated cases. The other, more probable extreme, $\alpha_j \times 1/10$, causes much smaller changes in the computed ion populations.

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